Time-resolved studies of photoinduced birefringence in azobenzene dye-doped polymer films

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We measured transient photoinduced birefringence (δn) in various azobenzene dye films by pumping with a nanosecond pulse at 532 nm and probing at 633 nm. The switch-on times for the photoinduced birefringence range from nanoseconds to milliseconds and are systematically related with the lowest optical transition energies for those films. Moreover, our results suggest that the transient photoinduced birefringence measurement is a convenient way to determine the relative energies of $\pi–\pi^*$ and $n–\pi^*$ states in azo-based materials. © 2008 Optical Society of America

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Azobenzene dyes and polymers have been extensively studied because of their abilities to switch light, record optical information, form surface relief gratings, etc. [1,2]. It is known that these properties derive from reversible trans–cis photoisomerization. The detailed process of photocyclization of trans–cis isomers of azo dyes can be ascribed to the following steps. (1) Linearly polarized light preferentially photoisomerizes the trans molecules that have their axes oriented along the light polarization to cis form; since trans and cis have different optical properties, anisotropy results. (2) Molecular angular redistribution when the cis form relaxes back to trans, and as the reorientation directions normally are random, anisotropy is statistically enhanced, which is the so-called dark reaction. (3) Through other thermal agitation processes, the material returns to the iso-tropic thermodynamic equilibrium state. Other than femtosecond time-scale studies on electronic properties [3–5], most experiments have been performed with cw irradiation, which mainly focuses on the static photophysical properties [6,7]; on the other hand, optical switching applications call for increasing the attention on the fast response time in azo materials, especially in the solid state, where the fairly limited work has been done [8,9].

Here we report on transient photoinduced birefringence (PIB) measurements on several azo dye films using a nanosecond laser source with a 20 ns time resolution; among these dye-doped polymers we observed that the photoinduced anisotropy response time ranges from within 20 ns to more than 200 μs. Our results show the response time of PIB to be systematically related to the size of the lowest optical transition energy. Furthermore, our results suggest that PIB effects can be used to discriminate between

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contributions from $\pi-\pi^*$ and $n-\pi^*$ transitions in the excited state manifold of azo dye molecules [4,5].

The azobenzene dyes studied in this work include Disperse Red 1 (DR1), Disperse Yellow 7 (DY7), Acid Blue, Sudan III (S3), Sudan III-2-Furoate (FS3), CPND5, Sudan Red 7B (SR7B), and Sudan Black B (SBB). The molecular structures are shown in Fig. 1. Samples were prepared by two methods. One method was standard spin coating from solutions of dye (FS3, S3, SBB, SR7B) doped (3 wt. % ratio to polymer) poly(methyl methacrylate) (6 wt. % in solution) in 1,2-dichloroethane onto a glass slide. The other was to put the homogeneous mixtures of dye (DY7, Acid Blue, CPND5) and glassy poly(acrylic TPD) (PATPD) polymer onto a glass substrate, along with a spacer (from ~ 10 to $\sim 100\,\mu m$) that was used to set the layer thickness. After slight heating to melt the polymer and careful removal of air bubbles, a top glass substrate was placed on the molten polymer [10]. Specifically, DR1 films were prepared by both methods for direct comparison, and the results did not depend on the film-forming technique.

The dynamics of PIB were investigated by the two-color pump–probe technique. A Nd:YAG laser at 532 nm with a 10 Hz repetition rate and an 8 ns pulse width served as the pump source, while a cw He–Ne laser at 632.8 nm was used as the probe beam. To achieve both high time resolution and high sensitivity at the same time, we used a DC-125 MHz photoreceiver (New Focus 1801 fs) and a fast sampling oscilloscope (Tektronic TDS2024B), with a measurement system time resolution of 20 ns achieved at a 10 Hz repetition rate; the pump fluence was about $80\,mJ/cm^2$. Pump and probe beams were carefully adjusted to obtain complete spatial overlap on the films. The sample film was placed between crossed polarizers that were perpendicular to the direction of the probe beam. The linear polarization of the pump beam was controlled by a half-wave plate, with the pump polarization adjusted to be at 45° relative to the probe beam. The transmittance through crossed polarizers can be expressed as $I_{out} = I_0 \sin^2(\pi\,\delta n\,d/\lambda_{probe})$ [8,11], where I_0 denotes the intensity of light through the polarizers when parallel, and d is sample thickness, allowing for calculation of the induced birefringence, δn. There was no time-dependent degradation of I_{out} observed in the measurement process.

All transmission spectra were measured with a Cary 5G UV-Vis-NIR spectrometer, and the lowest absorption maximum positions are summarized in Table 1. We grouped two sets of materials, six in (a) and two in (b), whose absorption maxima are at the blue side of, or very close to, and on the red side of the excitation wavelength (532 nm), respectively. Simply, for 532 nm excitation, all of the materials in (a) show PIB effects but with varying temporal response, while the materials in (b) showed no PIB.

We present the nanosecond time-scale dynamics of PIB in Fig. 2 in relation to the pump-pulse envelope. If we define the rise time τ as the time to reach 2/3 of the maximum value in Fig. 2, then τ for SR7B and DR1 both is 20 ns, i.e., limited by instrumental resolution. On the other hand, the maximum value for PIB in CPND5 is reached well after the pump pulse ends. Moreover, although the time resolution of the system is insufficient to delineate the difference between SR7B and DR1, it appears that τ of SR7B is shorter than that of DR1, as is τ of S3 (not shown here.) To avoid thermal effects on the dynamics analysis [8], various lower pump intensities as well as single pulse measurements were performed on DR1 and CPND5 films, and there was no difference observed in dynamics except for an expected increase of the noise level.

For better signal to noise, we intentionally increased the thickness of DY7 and FS3 films, which have small absorption coefficients at 532 nm, resulting in the linear transmission of DY7 and FS3 films being reduced to 65% and 56%, respectively, but there was still no nanosecond PIB response observed at the same irradiation intensity as the measurements shown in Fig. 2.

We extended our measurement to the millisecond domain for DY7 and FS3 and Fig. 3 shows the onset of the PIB process in DY7 and DR1, where the rise time of DY7 is $200\,\mu s$ and the PIB response of FS3 is similar to that of DY7.

The switch-off time constant is also important for some possible applications. The inset of Fig. 3 shows the PIB decay dynamics of DR1 and DY7. We cannot fit the dynamics of DR1 with a single exponential function, which also holds for SR7b, S3, and CPND5, indicating that the decay mechanisms are complex [8]. Following the same definition as that for the rise time, we obtain decay times for DR1, SR7B, S3, and CPND5 of 14, 13, 19, and 13 ms, respectively. This relatively fast decay in azo dye films could be useful for dynamic memory applications, such as holo-
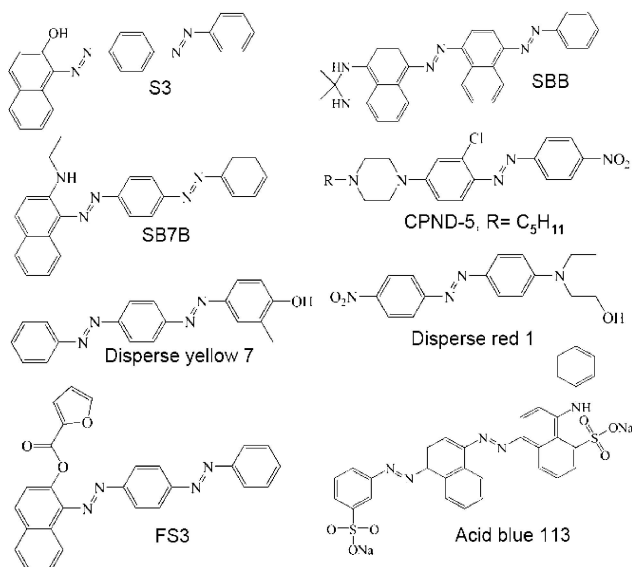

Fig. 1. Molecular structures of the eight azo dyes.

Table 1. Linear Transmittance at 532 nm, Lowest Optical Transition Energy, Rise Time for PIB Measurements, and δn in Various Azo Dye Films

Group	Sample	Linear transmittance at 532 nm (%)	Lowest absorption maximum (nm)	Rise time	δn (at $t = 20\,\mathrm{ns}$)
(a)	FS3	56	395	$\sim 200\,\mu s$	\
	DY7	65	407	$200\,\mu s$	\
	CPND5	2	471	50 ns	0.0014
	DR1	51	490	20 ns	0.0035
	S3	8	508	20 ns	0.0014
	SR7B	60	539	20 ns	0.0040
(b)	SBB	39	592	\	\
	Acid blue	35	650	\	\

graphic displays [12]. For completeness, we also present the decay dynamics of a DY7 film in the Fig. 3 inset; however, the DY7 response is relatively slow.

As summarized in Table 1, the rise time of PIB in azo dye films strongly correlates with the energy of the lowest optical absorption band. Basically, azo dyes with lower optical transition energies respond more quickly. However, when we consider the two dyes with their lowest energy absorption bands below the pump laser energy, Acid Blue (650 nm) and SBB (592 nm), there is no observable PIB pumped using either the 532 nm ns laser described above, or a 532 nm cw laser at intensities up to $1\,W/cm^2$, in contrast with the large induced birefringence in the other materials (Table 1). Therefore, we conclude that PIB effects are negligible in SBB and Acid Blue dye films excited by 532 nm lasers, despite the fact that the n–π^* state exists.

It is known that the n–π^* transition is generally fixed near 440 nm for a large number of azo dyes; on the contrary, the location of the π–π^* transition that is the main feature in the absorption spectrum can vary drastically between 300 to more than 600 nm because of the strong interactions among the π electrons. For example, in unsubstituted azo-

benzene, the π–π^* absorption near 320 nm is about 30 times stronger than the n–π^* transition at 440 nm, and the n–π^* state is the lowest excited state [4,5]. For SBB and Acid Blue, since the lowest absorption bands are far below the n–π^* transition, it is clear that the n–π^* state is not the lowest excited state. However, for some donor/acceptor substituted azobenzenes, like DR1, the push–pull interaction moves the π–π^* band to 500 nm, and the n–π^* transition is obscured by this strong band.

The identity of the lowest energy state in a given azo dye, π–π^* or n–π^*, is generally an open question [13–15]. Schmidt *et al.* reported femtosecond time-resolved transient absorption and fluorescence studies on 4-nitro-4'-(dimethylamino)-azobenzene (DMANAB) in toluene; the DMANAB is a push–pull substituted azobenzene with the π–π^* transition at around 450 nm. A model was proposed to explain the photoisomerization kinetics, accounting for the fact that the excitation of the π–π^* transition will generate a new charge distribution rapidly with large amplitude motion taking place away from the Franck–Condon equilibrium region. Upon return to the ground state, a subset of the excited molecules reverted to the initial trans form and the rest underwent photoexcitation to the cis form. It was assumed
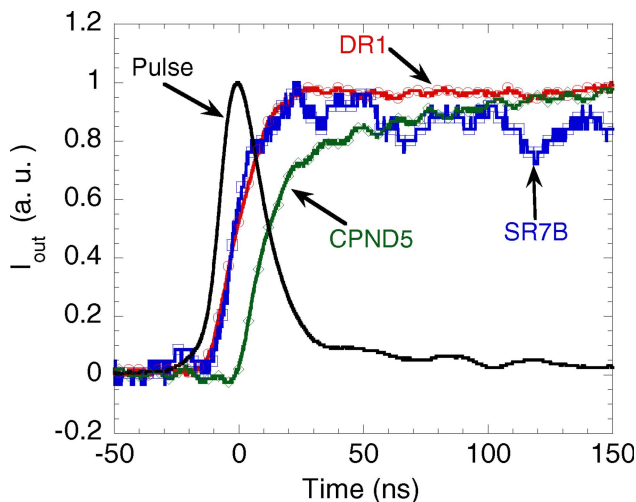

Fig. 2. (Color online) PIB rise dynamics of DR1, SR7B, and CPND5 films; the pulse trace measured with same configuration is also included.
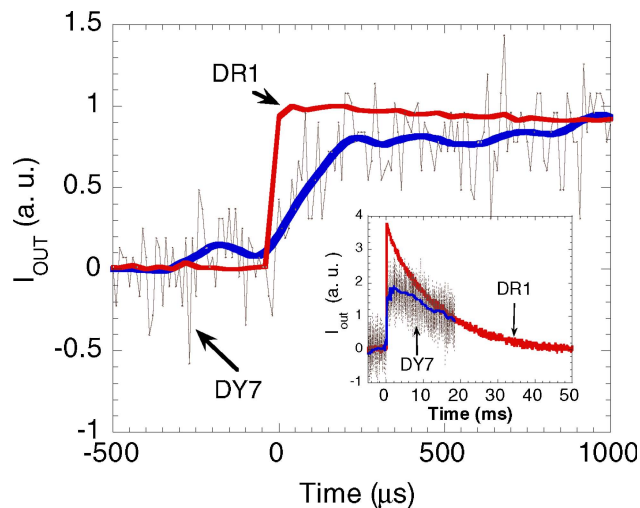

Fig. 3. (Color online) PIB rise dynamics of DY7 (line to guide eye) compared with DR1 with both decay dynamics given in the inset.

that the π–π^* transition was the lowest excited state and that strong push–pull substitution did not cause substantial changes in the photoexcitations dynamics. However, Poprawa-Smoluch et al. [13] studied DR1 in various solvents using femtosecond time-resolved transient absorption spectra and photoinduced dichroism dynamics, from which they concluded that the n–π^* transition was likely to be at the lowest energy, with the n–π^* state formed from the initially excited π–π^* state in less than 200 fs.

It has been proposed that there are two reaction mechanisms for trans–cis isomerization; one is the inversion mechanism under n–π^* excitation, and the other is the rotational mechanism under π–π^* excitation, similar to the isomerization of stilbene [16]. Because of steric hindrances in films and considering the results for SBB and Acid Blue, we conclude that the inversion mechanism dominates in our measurements [3], suggesting that the n–π^* states must be excited to lead to the PIB effects observed here. According to Kasha's rule, our measurements suggest that the n–π^* transition should be lower in energy than the π–π^* if PIB occurs. Therefore, PIB measurements could provide a straightforward way to determine whether the π–π^* or n–π^* state is lower in energy in azo materials. However, although our results suggest the internal conversion between π–π^* and n–π^* states plays an important role in the isomerization process, the response time dependence on the excited state energy is not yet understood. We suggest that energy transfer between the π–π^* and n–π^* states plays an important role, and multiwavelength pump and probe studies would be useful for further study of this problem.

In conclusion, we have measured photoinduced birefringence in various azo dye films and our results prove that the rise time of transient PIB correlates with absorption features that are determined from the molecular structure. The measured rise time varied over a wide range from nanoseconds to milliseconds when the materials were pumped at 532 nm, providing a way to obtain optical switching behavior with a chosen switching speed. Furthermore, our results suggest that the photoinduced birefringence measurement could be a convenient way to determine whether the π–π^* or n–π^* transitions in azo dye films is the lower excited state: if PIB is present then the n–π^* transition is the lowest energy state; otherwise, π–π^* is the lowest.

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